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STRUCTURALLY DIFFERENT DIVALENT METALLASILOXANES $[Mg\{O(Ph_2SiO)_2\}_2]$-μ-$(LiPy)$-μ-$\{(LiPy)_3(OH)(Cl)\}]$, $[Cr\{O(Ph_2SiO)_2\}_2$-μ-$(LiPy_2)_2]$, AND $[\{O(Ph_2SiO)_2\}Co\{O(Ph_2SiO)_3)\}$-$\mu$-$(LiPy_2)_2]$ FROM $Ph_2Si(OH)_2/2BuLi$ AND THE METAL DICHLORIDES

Isaac Abrahams, Michael Lazell, Majid Motevalli,
Charlotte K. Simon, and Alice C. Sullivan

Three structurally different metallasiloxanes were formed from reactions between in situ generated suspensions of $Ph_2Si(OH)_2/BuLi$ *(1:2) in tetrahydrofuran (THF) with, metal dichlorides* $MgCl_2{\cdot}2THF$, $CrCl_2$, *or* $CoCl_2$ *followed by toluene/Py (Py = pyridine) work-up. The X-ray structures are reported for:* $[Mg\{O(Ph_2SiO)_2\}_2]$-μ-$(LiPy)$-μ-$\{(LiPy)_3(OH)(Cl)\}$ *(1) incorporating two six-membered magnesiasiloxane rings and an* $MgLi_3O_3Cl$ *cubane fragment,* $[\{O(Ph_2SiO)_2\}Co\{O(Ph_2SiO)_3\}$-$\mu$-$(LiPy_2)_2]$ *(2) with both six- and eight-membered cobaltasiloxane rings and* $[Cr\{O(Ph_2SiO)_2\}_2$-μ-$(LiPy_2)_2]$ *(3) with two six-membered chromiasiloxane rings. Structure assembly in these cases is apparently dictated by the metal dichloride. The compound* $[\{O(Ph_2SiO)_2\}Mg\{O(Ph_2SiO)_3\}$-$\mu$-$(CoClPy)_2]{\cdot}Py$ *(4) is formed from* $[\{O(Ph_2SiO)_2\}Mg\{O(Ph_2SiO)_3\}$-$\mu$-$(LiPy_2)_2]$ *and* $CoCl_2$ *(1:2).*

A large number of coordination compounds bearing α,ω-siloxanediolate and silanediolate ligands $[O(R_2SiO)_n]^{2-}$ have been reported in recent years. These compounds are of interest as precatalysts for olefin polymerization (early ICI and AKZO patent literature) [1, 2], as precursors for metal oxide/silica materials and in connection with possible intermediates in anionic ring opening polymerization of cyclic siloxanes [3, 4]. In many cases [5] the final coordinated α,ω-siloxanediolate ligand is derived from *in situ* oligomerization of a precursor – silanediolate or siloxanediolate. For reactions involving the reagents $[O(Ph_2SiOM)_2]$ (M = Li, Na) and various precursor target metal compounds we have identified three distinct outcomes. Firstly, there is intact transfer of ligand to give compounds where the ligand adopts chelate-bridging coordination [6] (simple chelate or bridging modes were found in compounds derived from $O(Ph_2SiOH)_2$) [7, 8]. Secondly, transfer may occur with chain expansion to trisiloxanenediolate $^-OPh_2SiOSiPh_2SiOPh_2O^-$ which adopts chelate or chelate-bridging coordination [6]. Finally, the ligand can function as an oxo transfer reagent with elimination of cyclic trisiloxane [9].

Relatively high isolated crystalline product yields (>70% in terms of available silicon) can be obtained in each case, indicating a relatively high degree of product selectivity. Thus for the cases studied the pathways are apparently highly specific to particular reagent pairs.

In this paper we describe some coordination compounds derived from $Ph_2Si(OLi)_2$ and the metal dichlorides $MgCl_2{\cdot}2THF$, $CrCl_2$, and $CoCl_2$.

Department of Chemistry, Queen Mary and Westfield College, London E1 4NS, U.K.; e-mail: a.c.sullivan@qmw.ac.uk. Published in Khimiya Geterotsiklicheskikh Soedinenij, No. 8, pp. 1085-1097, August, 1999. Original article submitted June 4, 1999.

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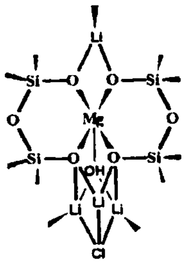
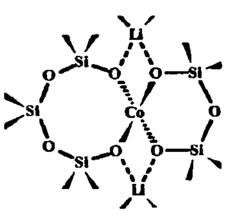
RESULTS AND DISCUSSION

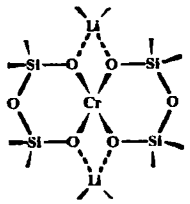
The diolate ligand $Ph_2SiO_2^{2-}$ is not always transferred intact from $Ph_2Si(OH)_2$ to target metal centers and the outcome varies with precursor metal compound e.g., intact transfer in $[Cp_2MOSiPh_2O]_2$ (M = Zr, Hf) [2, 10] from Cp_2MCl_2, and oligomerization in $[Ti(O(SiPh_2O)_4)_2]$ [11] from [Ti(OPr-*i*)$_4$] and in $[Ba_3(O(SiPh_2O)_2)_3]$ [12] from Ba/NH$_3$. However, we found that use of the reagents $Ph_2Si(OH)_2$ /BuLi (1:2), affected the outcome of reaction with Cp_2ZrCl_2 or $Cp*_2ZrCl_2$ in an unexpected way. These reactions gave the unexpected dimeric cyclozirconasiloxane products of $[(Cp/Cp*)_2ZrOSiPh_2OLiOH]_2$ where LiOH is incorporated within the chelate-bridging unit $[OSiPh_2OLi(OH)]^{2-}$ [13]. In fact the precise identity of the species formed on treatment of $Ph_2Si(OH)_2$ with BuLi in 1:2 molar ratio in THF is unknown; the combination of these two reagents gives a white suspension. This suspension failed to dissolve in various solvents (THF, toluene, or hexane) with overnight stirring at the reflux temperature. This lack of solubility inhibited our attempts to characterize this material. In contrast, treatment of $[O(Ph_2SiOH)_2]$ with BuLi in 1:2 molar ratio in THF gave a clear solution of the solvated reagent $[O(Ph_2SiOLi)_2)]\cdot(THF)_n$ [14]. In addition, the structures of the monolithium and monosodium derivatives of related silane diol *t*-Bu$_2$Si(OH)$_2$, [*t*-Bu$_2$Si(OH)(OLi).THF]$_4$ and [*t*-Bu$_2$Si(OH)(ONa).THF]$_6$ have been reported [15,16]. Despite the ill-defined nature of the product or products from $Ph_2Si(OH)_2$ /BuLi (1:2) we have used this *in situ* generated material in reactions with the metal dichlorides $MgCl_2$, $CrCl_2$ and $CoCl_2$ and isolated the compounds **1**, **2**, and **3** (molecular cores shown below).



(1)



(2)



(3)

We have previously reported on the reactions between these metal chlorides and the well-defined reagent $[O(Ph_2Si(OLi)_2)]$ and we now compare the products obtained using $Ph_2Si(OH)_2$/BuLi (1:2). The same procedure was used in each case and the yields of recrystallized products were 75, 52, and 47% for **1**, **2**, and **3**.

SYNTHESIS

[Mg{O(Ph$_2$SiO)$_2$}$_2$]-μ-(LiPy)-μ-{(LiPy)$_3$(OH)(Cl)] (1). Addition of $MgCl_2\cdot 2THF$ in THF to the dense white suspension {$Ph_2Si(OH)_2$/BuLi(1:2)} in THF in 1:5 molar ratio gave a clear yellow solution from which colorless crystalline [Mg{O(Ph$_2$SiO)$_2$}$_2$]-μ-(LiPy)-μ-{(LiPy)$_3$(OH)(Cl)] (**1**) (Fig. 1), was isolated after toluene-pyridine work-up. We previously reported on the synthesis of the lithium-bridged magnesiasiloxane compound [{O(Ph$_2$SiO)$_2$}Mg{O(Ph$_2$SiO)$_3$}-μ-{Li(THF)$_2$}$_2$] (**5**) from $MgCl_2\cdot 2THF$ and the well defined reagent $[O(Ph_2SiOLi)_2)]$ in 1:2 molar ratio [17]. Formation of compound **5** involved chain expansion of some of the starting disiloxanediolate giving both six- and eight-membered magnesiasiloxane rings in the product structure. The overall ratio of Mg:Si in compound **5** [{O(Ph$_2$SiO)$_2$}Mg{O(Ph$_2$SiO)$_3$}-μ-{Li(THF)$_2$}$_2$] is 1:5 and we used the 1:5 molar ratio $MgCl_2.2THF:Ph_2Si(OH)_2$ in the present case to see if compound **5** would form under these conditions. This was not the case. The compound [Mg{O(Ph$_2$SiO)$_2$}$_2$]-μ-(LiPy)-μ-{(LiPy)$_3$(OH)(Cl)}] (**1**) was isolated from this reaction in good (75%) yield. The structure incorporates oligomerized silanediolate in two six-membered magnesium disiloxanediolato rings as part of a lithium bridged spirocyclic unit that is a common structural motif of our work. Some 60% of the silicon available in the reaction is present in the disiloxanediolato ligands of the product. In compound **1**, however, there is an additional 4-membered ring present formally constructed

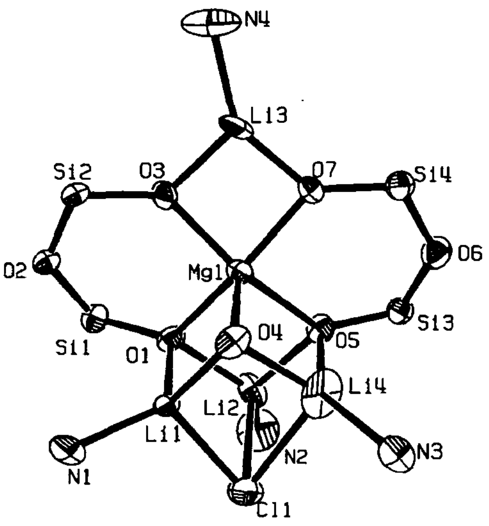


Fig. 1. Molecular structure of compound **1**.

from an equivalent each of LiOH and LiCl coordinated to one of the 4-membered magnesialithiooxane, MgO(Si)LiO(Si), rings in the molecule. Hydroxide is coordinated to the magnesium atom and chloride to lithium atom. Thus a cubane fragment is built into one side of the lithium bridged spirocyclic unit. This is the second compound we have derived from $Ph_2Si(OH)_2$ /BuLi(1:2) where LiOH has been incorporated in the structure. We previously reported on isolation of $[Cp^*_2ZrOSiPh_2OLiOH]_2$ from $Cp^*_2ZrCl_2$ and $Ph_2Si(OH)_2$/BuLi(1:2) in ~30% yield as mentioned above. The appearance of single resonances in both the ^{7}Li and ^{29}Si solution phase spectra of **1** and the presence of two distinct silicon atom environments and several distinct lithium atom environments in the solid state structure of **1** indicates that the solid state structure of compound **1** is either not retained or is fluxional in solution. The hydroxyl proton could not be unambiguously assigned from the proton NMR spectrum but there is a weak band at 3400 cm^{-1} in the infrared spectrum.

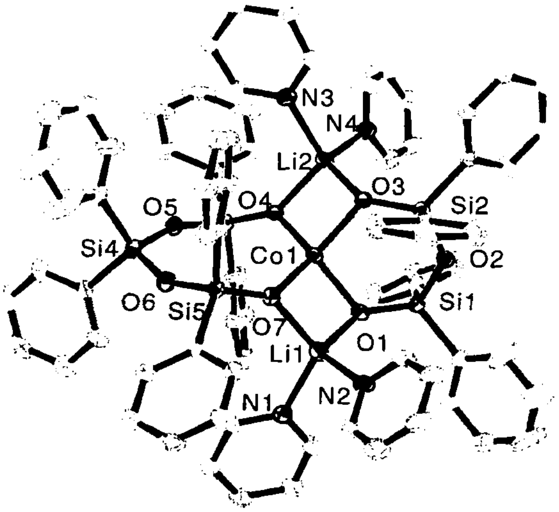


Fig. 2. Molecular structure of compound **2**.

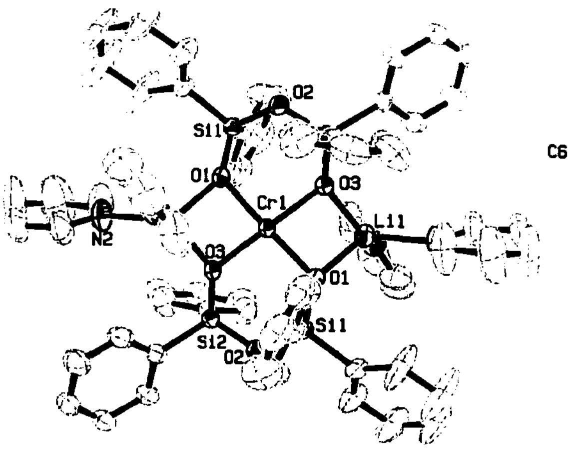


Fig. 3. Molecular structure of compound **3**

$[\{O(Ph_2SiO)_2\}Co\{O(Ph_2SiO)_3\}$-μ-$(LiPy_2)_2]$ (2). The combination of $MgCl_2{\cdot}2THF$ and $\{Ph_2Si(OH)_2/BuLi(1{:}2)\}$ in 1:5 molar ratio did not lead to $[\{O(Ph_2SiO)_2\}Mg\{O(Ph_2SiO)_3\}$-μ-$\{Li(THF)_2\}_2]$ (**5**) as discussed above but surprisingly a similar reaction between $CoCl_2$ and $\{Ph_2Si(OH)_2/BuLi(1{:}2)\}$ in 1:5 molar ratio did give the analogous cobalt compound $[\{O(Ph_2SiO)_2\}Co\{O(Ph_2SiO)_3\}$-μ-$(LiPy_2)_2]$ (**2**), (Fig. 2), with the slight difference that in **5** the bridging lithium atom is solvated by THF while in **2** the bridging lithium is solvated by pyridine. We had previously reported the related spirocyclic species $[Co\{O(Ph_2SiO)_2\}_2$-μ-$(LiTMEDA)_2]$ [18] with two six-membered cobaltasiloxane rings from the reaction between $CoCl_2$ and $[O(Ph_2Si(OLi)_2)]$. There are no similar examples of cobaltasiloxanes with both 6- and 8-membered rings. We note here that treatment of $[\{O(Ph_2SiO)_2\}Mg\{O(Ph_2SiO)_3\}$-μ-$\{Li(THF)_2\}_2]$ with $CoCl_2$ in 1:2 molar ratio gives a blue crystalline product after toluene-pyridine work-up. The bridging lithium atoms in $[\{O(Ph_2SiO)_2\}Mg\{O(Ph_2SiO)_3\}$-μ-$\{Li(THF)_2\}_2]$ have been replaced and elemental analysis of the new compound is in close agreement with the formulation $[\{O(Ph_2SiO)_2\}Mg\{(OPh_2Si)_3O)_2\}$-μ-$(CoClPy)_2]{\cdot}Py$ (**4**). We have previously reported on exchange of the metal ions in both bridging and spiro sites in the related compound $[Co\{O(Ph_2SiO)_2\}_2$-μ-$\{Li(THF)_2\}_2]$ [19].

$Cr\{O(Ph_2SiO)_2\}_2$-μ-$(LiPy_2)_2]$ (3). A lithium bridged spirocyclic compound $[Cr\{O(Ph_2SiO)_2\}_2$-μ-$(LiPy_2)_2]$ (**3**) (Fig. 3), having two six-membered chromiadisiloxane rings and no cubane fragment as in **1**, was obtained in the reaction between $CrCl_2$ and $\{Ph_2Si(OH)_2/BuLi(1{:}2)\}$ in 1:5 molar ratio. We have reported earlier [20] on the analogous sodium bridged compound $[Cr\{O(Ph_2SiO)_2\}_2$-μ-$\{Na(THF)_2\}_2]$ from $[O(Ph_2SiONa)_2]$ and $CrCl_2$ but we were unable to isolate the lithium bridged species from a similar reaction using $[O(Ph_2SiOLi)_2]$ in place of the disodium reagent $[O(Ph_2SiONa)_2]$.

X-RAY CRYSTALLOGRAPHY

Crystallographic data for compounds **1**, **2**, and **3** are summarized in Table 1.

Structural Features of $[Mg\{O(Ph_2SiO)_2\}_2$-μ-$(LiPy)$-μ-$\{(LiPy)_3(OH)(Cl)]$ (1). The molecular structure of **1** is shown in Fig. 1 and bond lengths and angles in Table 2. The structure was solved by the Patterson method in the centrosymmetric space group Pnma (No. 62). However, the refined structure in this space group indicated significant positional disorder on the pyridine rings located on the mirror plane. The coordinates were transformed to the non-centrosymmetric system Pn21a (No. 33) and an improved refinement obtained with ordered pyridine rings. However, in consequence of the presence of a pseudo-mirror plane in the molecule the esds on bond distances and angles, particularly those associated with the pyridine groups, remain high. The compound adopts an unusual variation of the lithium bridged spirocyclic motif which is commonly obtained from reactions between metal dichlorides and the reagent $[O(Ph_2SiOLi)_2]$. The common motif has been extended here by addition of LiOH

TABLE 1. Crystallographic Data for Compounds **1**, **2**·Toluene, and **3**

	Compound **1**	Compound **2**	Compound **3**
Empirical formula	$C_{68}H_{61}ClLi_4MgN_4O_7Si_4$	$C_{87}H_{78}CoLi_2N_4O_7Si_5$	$C_{68}H_{60}CrLi_2N_4O_6Si_4$
Formula weight	1244.37	1504.79	1207.44
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	Pn21a	P BAR1	P BAR1
Unit cell dimensions	a = 21.928(4) Å; α = 90° b = 24.406(5) Å; β = 90° c = 13.328(3) Å; γ = 90°	a = 14.103(4) Å; α = 88.30(1)° b = 14.620(5) Å; β = 81.36(2)° c = 20.510(1) Å; γ = 72.74(1)°.	a = 13.157(3) Å; α = 86.24(3)° b = 13.489(3) Å; β = 75.91(3)° c = 21.553(4) Å; γ = 62.04(3)°
Volume	7132.8(25) Å^3	3992.1(18) A^3	3271.7(12) Å^3
Z	4	2	2
Density (calculated)	1.160 Mg/m^3	1.252 Mg/m^3	1.226 Mg/m^3
Absorption coefficient	0.180 mm^{-1}	0.347 mm^{-1}	0.301 mm^{-1}
F(000)	2592	1574	1260
Crystal size	0.4×0.2 ×0.18 mm	0.5×0.4×0.18 mm	0.40 ×0.35 ×0.28 mm
Theta range for data collection	1.67 to 24.98°.	1.76 to 24.89°.	1.71 to 25.00°.
Index ranges	$0<=h<=26$, $0<=k<=27$, $0<=l<=15$	$-15\le h\le 16$, $-13\le k\le 16$, $-23\le l\le 22$	$-14\le h\le 15$, $-15\le k\le 16$, $0\le l\le 25$
Reflections collected	6388	14985	12238
Independent reflections	6385 [R_{int} = 0.0000]	10135 [R_{int} = 0.0857]	11478 [R_{int} = 0.0126]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6385 / 0 / 661	10135 / 0 / 858	11478 / 0 / 685
Goodness of-fit on F^2	0.889	0.709	0.952
Final R indices [I>2σ(I)]	R_1 = 0.0977, wR_2 = 0.2591	R_1 = 0.0548, wR_2 = 0.1063	R_1 = 0.0627, wR_2 = 0.1860
R indices (all data)	R_1 = 0.1689, wR_2 = 0.3146	R_1 = 0.1108, wR_2 = 0.1160	R_1 = 0.1052, wR_2 = 0.2065
Largest diff. peak and hole	1.755 and -0.437 e.Å^{-3}	0.462 and -0.318 e.Å^{-3}	1.063 and -0.385 e.Å^{-3}

and LiCl to give a built-in cubane fragment on one side of the molecule with the hydroxyl coordinated to two lithium atoms and magnesium atom and the chloride coordinated to three lithium atoms. The bond distances and angles within the coplanar magnesiadisiloxanediolate 6-membered rings are similar to those previously found for the 6-membered ring in **5**. Tetrahedral geometry is maintained at silicon. Magnesium atom has approximately square pyramidal stereochemistry and sits slightly below the plane of the equatorial ligating oxygens. The cubane fragment shows some distortion at the site occupied by chlorine where the Li-Cl-Li angles in the range 69.1(7)-72.6(8)° are small (even allowing for the high esds) compared to the angles at other corners of the cube. Likewise despite the high esds there is some asymmetry about the coordination of Py to $Li_{(3)}$ with $N_{(4)}$–$Li_{(3)}$–$O_{(7)}$ 141.9(19) and $N_{(4)}$–$Li_{(3)}$–$O_{(3)}$ 122.9(18). However, there are no intermolecular van der Waals interactions that may account for either of these features but there is an intramolecular contact (between $C_{(58)}$ on the pyridine ring attached to $Li_{(2)}$ and $Cl_{(1)}$ (3.41 Å) which may indicate existence of some hydrogen bonding $Cl_{(1)}$–$H_{(58)}$.

TABLE 2. Bond Lengths and Angles for Compound 1

Bond	Bond length, Å	Bond	Bond length, Å
Mg$_{(1)}$–O$_{(4)}$	1.989(6)	Si$_{(4)}$–C$_{(37)}$	1.889(9)
Mg$_{(1)}$–O$_{(3)}$	2.016(11)	Si$_{(4)}$–C$_{(43)}$	1.984(11)
Mg$_{(1)}$–O$_{(7)}$	2.019(10)	O$_{(1)}$–Li$_{(2)}$	1.94(3)
Mg$_{(1)}$–O$_{(5)}$	2.059(10)	O$_{(1)}$–Li$_{(1)}$	2.13(3)
Mg$_{(1)}$–O$_{(1)}$	2.122(10)	O$_{(3)}$–Li$_{(3)}$	1.87(3)
Si$_{(1)}$–O$_{(1)}$	1.609(10)	O$_{(4)}$–Li$_{(1)}$	1.89(2)
Si$_{(1)}$–O$_{(2)}$	1.640(10)	O$_{(4)}$–Li$_{(4)}$	1.99(4)
Si$_{(1)}$–C$_{(1)}$	1.861(8)	O$_{(4)}$–H$_{(4)}$	0.98
Si$_{(1)}$–C$_{(7)}$	1.887(10)	O$_{(5)}$–Li$_{(2)}$	1.96(2)
Si$_{(2)}$–O$_{(3)}$	1.558(10)	O$_{(5)}$–Li$_{(4)}$	2.03(3)
Si$_{(2)}$–O$_{(2)}$	1.647(10)	O$_{(7)}$–Li$_{(3)}$	1.80(3)
Si$_{(2)}$–C$_{(19)}$	1.843(9)	Cl$_{(1)}$–Li$_{(1)}$	2.37(2)
Si$_{(2)}$–C$_{(13)}$	1.897(9)	Cl$_{(1)}$–Li$_{(2)}$	2.42(2)
Si$_{(3)}$–O$_{(5)}$	1.584(10)	Cl$_{(1)}$–Li$_{(4)}$	2.52(4)
Si$_{(3)}$–O$_{(6)}$	1.636(11)	Li$_{(1)}$–N$_{(1)}$	2.00(2)
Si$_{(3)}$–C$_{(31)}$	1.852(10)	Li$_{(2)}$–N$_{(2)}$	2.04(2)
Si$_{(3)}$–C$_{(25)}$	1.903(8)	Li$_{(3)}$–N$_{(4)}$	2.06(2)
Si$_{(4)}$–O$_{(7)}$	1.615(10)	Li$_{(4)}$–N$_{(3)}$	2.09(2)
Si$_{(4)}$–O$_{(6)}$	1.624(11)		

Bond	Bond angle, deg.	Bond	Bond angle, deg.
O$_{(4)}$–Mg$_{(1)}$–O$_{(3)}$	114.6(5)	Li$_{(3)}$–O$_{(3)}$–Mg$_{(1)}$	90.3(9)
O$_{(4)}$–Mg$_{(1)}$–O$_{(7)}$	113.5(5)	Li$_{(1)}$–O$_{(4)}$–Mg$_{(1)}$	96.7(8)
O$_{(3)}$–Mg$_{(1)}$–O$_{(7)}$	83.4(2)	Li$_{(1)}$–O$_{(4)}$–Li$_{(4)}$	91.9(9)
O$_{(4)}$–Mg$_{(1)}$–O$_{(5)}$	89.8(4)	Mg$_{(1)}$–O$_{(4)}$–Li$_{(4)}$	91.2(8)
O$_{(3)}$–Mg$_{(1)}$–O$_{(5)}$	155.2(4)	Li$_{(1)}$–O$_{(4)}$–H$_{(4)}$	122.8(8)
O$_{(7)}$–Mg$_{(1)}$–O$_{(5)}$	91.1(4)	Mg$_{(1)}$–O$_{(4)}$–H$_{(4)}$	122.9(2)
O$_{(4)}$–Mg$_{(1)}$–O$_{(1)}$	87.3(4)	Li$_{(4)}$–O$_{(4)}$–H$_{(4)}$	122.9(7)
O$_{(3)}$–Mg$_{(1)}$–O$_{(1)}$	92.3(4)	Si$_{(3)}$–O$_{(5)}$–Li$_{(2)}$	129.4(9)
O$_{(7)}$–Mg$_{(1)}$–O$_{(1)}$	158.6(4)	Si$_{(3)}$–O$_{(5)}$–Li$_{(4)}$	109.8(10)
O$_{(5)}$–Mg$_{(1)}$–O$_{(1)}$	84.0(2)	Li$_{(2)}$–O$_{(5)}$–Li$_{(4)}$	89.3(12)
Si$_{(1)}$–O$_{(1)}$–Li$_{(2)}$	133.0(8)	Si$_{(3)}$–O$_{(5)}$–Mg$_{(1)}$	132.8(6)
Si$_{(1)}$–O$_{(1)}$–Li$_{(1)}$	117.6(7)	Li$_{(2)}$–O$_{(5)}$–Mg$_{(1)}$	92.7(9)
Li$_{(2)}$–O$_{(1)}$–Li$_{(1)}$	88.9(8)	Li$_{(4)}$–O$_{(5)}$–Mg$_{(1)}$	88.0(11)
Si$_{(1)}$–O$_{(1)}$–Mg$_{(1)}$	126.3(5)	Si$_{(4)}$–O$_{(6)}$–Si$_{(3)}$	131.7(7)
Li$_{(2)}$–O$_{(1)}$–Mg$_{(1)}$	91.2(7)	Si$_{(4)}$–O$_{(7)}$–Li$_{(3)}$	135.0(9)
Li$_{(1)}$–O$_{(1)}$–Mg$_{(1)}$	86.1(6)	Si$_{(4)}$–O$_{(7)}$–Mg$_{(1)}$	132.8(6)
Si$_{(1)}$–O$_{(2)}$–Si$_{(2)}$	128.8(6)	Li$_{(3)}$–O$_{(7)}$–Mg$_{(1)}$	92.0(8)
Si$_{(2)}$–O$_{(3)}$–Li$_{(3)}$	134.9(10)	O$_{(1)}$–Li$_{(2)}$–Cl$_{(1)}$	99.5(9)
Si$_{(2)}$–O$_{(3)}$–Mg$_{(1)}$	133.9(6)	O$_{(5)}$–Li$_{(2)}$–Cl$_{(1)}$	103.0(10)
O$_{(1)}$–Si$_{(1)}$–O$_{(2)}$	112.9(5)	N$_{(2)}$–Li$_{(2)}$–Cl$_{(1)}$	103.5(7)
O$_{(3)}$–Si$_{(2)}$–O$_{(2)}$	111.2(5)	O$_{(7)}$–Li$_{(3)}$–O$_{(3)}$	94.0(7)
O$_{(5)}$–Si$_{(3)}$–O$_{(6)}$	109.5(6)	O$_{(7)}$–Li$_{(3)}$–N$_{(4)}$	142.1(18)
O$_{(7)}$–Si$_{(4)}$–O$_{(6)}$	110.4(5)	O$_{(3)}$–Li$_{(3)}$–N$_{(4)}$	122.8(17)
O$_{(4)}$–Li$_{(1)}$–N$_{(1)}$	127.2(13)	O$_{(4)}$–Li$_{(4)}$–O$_{(5)}$	90.5(11)
O$_{(4)}$–Li$_{(1)}$–O$_{(1)}$	89.7(9)	O$_{(4)}$–Li$_{(4)}$–N$_{(3)}$	121.1(14)
N$_{(1)}$–Li$_{(1)}$–O$_{(1)}$	123.7(10)	O$_{(5)}$–Li$_{(4)}$–N$_{(3)}$	140.8(18)
O$_{(4)}$–Li$_{(1)}$–Cl$_{(1)}$	102.8(9)	O$_{(4)}$–Li$_{(4)}$–Cl$_{(1)}$	95.2(13)
N$_{(1)}$–Li$_{(1)}$–Cl$_{(1)}$	111.6(9)	O$_{(5)}$–Li$_{(4)}$–Cl$_{(1)}$	97.6(11)
O$_{(1)}$–Li$_{(1)}$–Cl$_{(1)}$	95.8(9)	N$_{(3)}$–Li$_{(4)}$–Cl$_{(1)}$	101.4(14)
O$_{(1)}$–Li$_{(2)}$–O$_{(5)}$	91.8(6)	Li$_{(1)}$–Cl$_{(1)}$–Li$_{(2)}$	72.9(8)
O$_{(1)}$–Li$_{(2)}$–N$_{(2)}$	125.6(16)	Li$_{(1)}$–Cl$_{(1)}$–Li$_{(4)}$	69.5(7)
O$_{(5)}$–Li$_{(2)}$–N$_{(2)}$	128.6(14)	Li$_{(2)}$–Cl$_{(1)}$–Li$_{(4)}$	69.1(7)

TABLE 3. Bond Lengths [Å] and Angles [deg.] for Compound **2** with Some Values in Parentheses for Compound **5** for Comparison

Bond	Bond length, Å	Bond	Bond length, Å
$Co_{(1)}-O_{(4)}$	1.966(3)	$Si_{(4)}-O_{(5)}$	1.622(4)(1.600(3))
$Co_{(1)}-O_{(7)}$	1.969(3)	$Si_{(5)}-O_{(7)}$	1.598(4)(1.586(3))
$Co_{(1)}-O_{(1)}$	1.979(3)	$Si_{(5)}-O_{(6)}$	1.649(4)(1.638(3))
$Co_{(1)}-O_{(3)}$	1.997(3)	$N_{(2)}-Li_{(1)}$#2	2.121(11)(2.066(8))
$Si_{(1)}-O_{(1)}$	1.607(4)(1.600(3))	$Li_{(1)}-O_{(1)}$	1.882(10)(1.937(5))
$Si_{(1)}-O_{(2)}$	1.641(3)(1.643(3))	$Li_{(1)}-O_{(7)}$	1.958(9)(1.991(8))
$Si_{(1)}-C_{(1)}$	1.888(3)	$Li_{(1)}-N_{(1)}$	2.101(10)(2.053(9))
$Si_{(1)}-C_{(7)}$	1.914(3)	$Li_{(1)}-N_{(2)}$#1	2.121(11)(2.066(8))
$Si_{(2)}-O_{(3)}$	1.607(3)(1.596(3))	$Li_{(2)}-O_{(3)}$	1.875(9)(1.925(8))
$Si_{(2)}-O_{(2)}$	1.647(3)(1.641(3))	$Li_{(2)}-O_{(4)}$	1.967(9)(2.000(9))
$Si_{(3)}-O_{(4)}$	1.600(4)(1.587(3))	$Li_{(2)}-N_{(4)}$	2.074(10)(2.011(9))
$Si_{(3)}-O_{(5)}$	1.635(4)(1.641(3))	$Li_{(2)}-N_{(3)}$	2.112(9)(1.998(9))
$Si_{(4)}-O_{(6)}$	1.618(4)(1.612(3))		

Bond	Bond angle, deg.	Bond	Bond angle, deg.
$O_{(4)}-Co_{(1)}-O_{(7)}$	114.71(14)(114.85(14))	$Si_{(2)}-O_{(3)}-Li_{(2)}$	141.9(3)
$O_{(4)}-Co_{(1)}-O_{(1)}$	134.28(15)(126.62(14))	$Si_{(2)}-O_{(3)}-Co_{(1)}$	121.27(16)
$O_{(7)}-Co_{(1)}-O_{(1)}$	89.49(13)(94.14(14))	$Li_{(2)}-O_{(3)}-Co_{(1)}$	90.5(3)
$O_{(4)}-Co_{(1)}-O_{(3)}$	88.56(13)(93.86(14))	$Si_{(3)}-O_{(4)}-Co_{(1)}$	132.39(19)
$O_{(7)}-Co_{(1)}-O_{(3)}$	132.33(14)(125.6(2))	$Si_{(3)}-O_{(4)}-Li_{(2)}$	138.8(3)
$O_{(1)}-Co_{(1)}-O_{(3)}$	103.35(13)(104.53(14))	$Co_{(1)}-O_{(4)}-Li_{(2)}$	88.8(3)
$O_{(1)}-Si_{(1)}-O_{(2))}$	111.71(19)	$Si_{(4)}-O_{(6)}-Si_{(5)}$	150.4(2)
$O_{(3)}-Si_{(2)}-O_{(2)}$	111.26(19)	$Si_{(5)}-O_{(7)}-Li_{(1)}$	135.7(4)
$O_{(4)}-Si_{(3)}-O_{(5)}$	111.6(2)	$Si_{(5)}-O_{(7)}-Co_{(1)}$	136.12(19)
$O_{(6)}-Si_{(4)}-O_{(5)}$	110.84(19)	$Li_{(1)}-O_{(7)}-Co_{(1}$	88.0(3)
$O_{(7)}-Si_{(5)}-O_{(6)}$	112.1(2)	$Si_{(1)}-O_{(1)}-Li_{(1)}$	142.0(4)
$O_{(1)}-Li_{(1)}-O_{(7)}$	92.7(4)	$Si_{(1)}-O_{(1)}-Co_{(1)}$	120.67(18)
$O_{(1)}-Li_{(1)}-N_{(1)}$	118.4(5)	$Li_{(1)}-O_{(1)}-Co_{(1)}$	89.8(3)
$O_{(7)}-Li_{(1)}-N_{(1)}$	115.5(5)	$Si_{(1)}-O_{(2)}-Si_{(2)}$	131.9(2)
$O_{(1)}-Li_{(1)}-N_{(2)}$#1	111.2(5)	$Si_{(2)}-O_{(3)}-Li_{(2)}$	141.9(3)
$O_{(7)}-Li_{(1)}-N_{(2)}$#1	118.9(5)	$Si_{(2)}-O_{(3)}-Co_{(1)}$	121.27(16)
$N_{(1)}-Li_{(1)}-N_{(2)}$#1	101.3(4)	$Li_{(2)}-O_{(3)}-Co_{(1)}$	90.5(3)
$O_{(3)}-Li_{(2)}-O_{(4)}$	92.1(4)	$Si_{(3)}-O_{(4)}-Co_{(1)}$	132.39(19)
$O_{(3)}-Li_{(2)}-N_{(4)}$	112.6(5)	$Si_{(3)}-O_{(4)}-Li_{(2)}$	138.8(3)
$O_{(4)}-Li_{(2)}-N_{(4)}$	121.7(5)	$Co_{(1)}-O_{(4)}-Li_{(2)}$	88.8(3)
$O_{(3)}-Li_{(2)}-N_{(3)}$	119.9(5)	$Si_{(4)}-O_{(5)}-Si_{(3)}$	156.0(2)
$O_{(4)}-Li_{(2)}-N_{(3)}$	111.1(4)	$Si_{(4)}-O_{(6)}-Si_{(5)}$	150.4(2)
$N_{(4)}-Li_{(2)}-N_{(3)}$	100.9(4)	$Si_{(5)}-O_{(7)}-Li_{(1)}$	135.7(4)
$Si_{(1)}-O_{(1)}-Li_{(1)}$	142.0(4)	$Si_{(5)}-O_{(7)}-Co_{(1)}$	136.12(19)
$Si_{(1)}-O_{(1)}-Co_{(1)}$	120.67(18)	$Li_{(1)}-O_{(7)}-Co_{(1}$	88.0(3)
$Li_{(1)}-O_{(1)}-Co_{(1)}$	89.8(3)	$Li_{(1)}-Co_{(1)}-Li_{(2)}$	172.0(3)
$Si_{(1)}-O_{(2)}-Si_{(2)}$	131.9(2)		

Symmetry transformations used to generate equivalent atoms:
#1 $x,y+1,z$ #2 $x,y-1,z$ #3 $-x,-y+2,-z$ #4 $-x,-y+2,-z+1$

Structural Features of [{O(Ph_2SiO)$_2$}Co{O(Ph_2SiO)$_3$}-μ-($LiPy_2$)$_2$] (2). The molecular structure of **2** is shown in Fig. 2 and bond lengths and angles in Table 3. The four Co-O distances are very similar and close to those in the related compound [Co{O(Ph_2SiO)$_2$}$_2$-μ-(LiTMEDA)$_2$] [18] where there are two six-membered cobaltasiloxane rings. The cobalt atom is at the center of a flattened tetrahedron. The bond angles around the central cobalt atom vary in precisely the same way as those in the related magnesium compound **5** [17]. The *trans*-O–Co–O angles are about 7° wider and the *cis*-O–Co–O angles (within the CoO_2Li rings) are some 5° smaller than

TABLE 4. Bond Lengths and Angles for Compound **3** with Comparative Values in Parentheses for $[Cr\{O(Ph_2SiO)_2\}_2\text{-}\mu\text{-}\{Na(THF)_2\}_2]$

Bond	Bond length, Å	Bond	Bond length, Å
$\mathrm{Cr_{(1)}{-}O_{(1)}\#1}$	1.994(2) (1.987(7))	$\mathrm{Si_{(3)}{-}O_{(5)}}$	1.644(3)
$\mathrm{Cr_{(1)}{-}O_{(1)}}$	1.994(2)	$\mathrm{Si_{(3)}{-}C_{(35)}}$	1.885(3)
$\mathrm{Cr_{(1)}{-}O_{(3)}\#1}$	2.012(3) (1.985(6))	$\mathrm{Si_{(3)}{-}C_{(41)}}$	1.890(2)
$\mathrm{Cr_{(1)}{-}O_{(3)}}$	2.012(3)	$\mathrm{Si_{(4)}{-}O_{(6)}}$	1.597(3)
$\mathrm{Cr_{(2)}{-}O_{(4)}\#2}$	1.983(2)	$\mathrm{Si_{(4)}{-}O_{(5)}}$	1.643(3)
$\mathrm{Cr_{(2)}{-}O_{(4)}}$	1.983(2)	$\mathrm{Si_{(4)}{-}C_{(47)}}$	1.880(2)
$\mathrm{Cr_{(2)}{-}O_{(6)}}$	1.999(2)	$\mathrm{Si_{(4)}{-}C_{(53)}}$	1.889(3)
$\mathrm{Cr_{(2)}{-}O_{(6)}\#2}$	1.999(2)	$\mathrm{Li_{(1)}{-}O_{(3)}}$	1.892(7)
$\mathrm{Si_{(1)}{-}O_{(1)}}$	1.590(3) (1.589(6))	$\mathrm{Li_{(1)}{-}O_{(1)}\#1}$	1.905(8)
$\mathrm{Si_{(1)}{-}O_{(2)}}$	1.646(3)	$\mathrm{Li_{(1)}{-}N_{(2)}}$	2.079(8)
$\mathrm{Si_{(1)}{-}C_{(7)}}$	1.876(3)	$\mathrm{Li_{(1)}{-}N_{(1)}}$	2.081(8)
$\mathrm{Si_{(1)}{-}C_{(1)}}$	1.883(3)	$\mathrm{Li_{(2)}{-}O_{(4)}\#2}$	1.870(8)
$\mathrm{Si_{(2)}{-}O_{(3)}}$	1.598(3)	$\mathrm{Li_{(2)}{-}O_{(6)}}$	1.903(7)
$\mathrm{Si_{(2)}{-}O_{(2)}}$	1.642(3)	$\mathrm{Li_{(2)}{-}N_{(3)}\#2}$	2.072(8)
$\mathrm{Si_{(2)}{-}C_{(19)}}$	1.894(2)	$\mathrm{Li_{(2)}{-}N_{(4)}\#2}$	2.085(8)
$\mathrm{Si_{(2)}{-}C_{(13)}}$	1.901(3)	$\mathrm{O_{(1)}{-}Li_{(1)}\#1}$	1.905(8)
$\mathrm{Si_{(3)}{-}O_{(4)}}$	1.601(3)	$\mathrm{O_{(4)}{-}Li_{(2)}\#2}$	1.870(8)

Bond	Bond angle, deg.	Bond	Bond angle, deg.
$\mathrm{O_{(1)}\#1{-}Cr_{(1)}{-}O_{(1)}}$	180.0 (180.0(3))	$\mathrm{O_{(1)}\#1{-}Li_{(1)}{-}N_{(1)}}$	108.8(4)
$\mathrm{O_{(1)}\#1{-}Cr_{(1)}{-}O_{(3)}\#1}$	94.70(11)(93.2(3))	$\mathrm{N_{(2)}{-}Li_{(1)}{-}N_{(1)}}$	103.0(3)
$\mathrm{O_{(1)}{-}Cr_{(1)}{-}O_{(3)}\#1}$	85.30(11)(86.8(3))	$\mathrm{O_{(4)}\#2{-}Li_{(2)}{-}O_{(6)}}$	91.4(3)
$\mathrm{O_{(1)}\#1{-}Cr_{(1)}{-}O_{(3)}}$	85.30(11)	$\mathrm{O_{(4)}\#2{-}Li_{(2)}{-}N_{(3)}\#2}$	117.2(4)
$\mathrm{O_{(1)}{-}Cr_{(1)}{-}O_{(3)}}$	94.70(11)	$\mathrm{O_{(6)}{-}Li_{(2)}{-}N_{(3)}\#2}$	118.7(4)
$\mathrm{O_{(3)}\#1{-}Cr_{(1)}{-}O_{(3)}}$	180.0	$\mathrm{O_{(4)}\#2{-}Li_{(2)}{-}N_{(4)}\#2}$	106.2(4)
$\mathrm{Li_{(1)}{-}Cr_{(1)}{-}Li_{(1)}\#1}$	179.999(1)	$\mathrm{O_{(6)}{-}Li_{(2)}{-}N_{(4)}\#2}$	108.4(4)
$\mathrm{O_{(4)}\#2{-}Cr_{(2)}{-}O_{(4)}}$	180.0	$\mathrm{N_{(3)}\#2{-}Li_{(2)}{-}N_{g}\#2}$	112.7(4)
$\mathrm{O_{(4)}\#2{-}Cr_{(2)}{-}O_{(6)}}$	85.40(10)	$\mathrm{Si_{(1)}{-}O_{(1)}{-}Li_{(1)}\#1}$	146.6(3)
$\mathrm{O_{(4)}{-}Cr_{(2)}{-}O_{(6)}}$	94.60(10)	$\mathrm{Si_{(1)}{-}O_{(1)}{-}Cr_{(1)}}$	122.8(2)
$\mathrm{O_{(4)}\#2{-}Cr_{(2)}{-}O_{(6)}\#2}$	94.60(10)	$\mathrm{Li_{(1)}\#1{-}O_{(1)}{-}Cr_{(1)}}$	90.3(2)
$\mathrm{O_{(4)}{-}Cr_{(2)}{-}O_{(6)}\#2}$	85.40(10)	$\mathrm{Si_{(2)}{-}O_{(2)}{-}Si_{(1)}}$	124.3(2)
$\mathrm{O_{(6)}{-}Cr_{(2)}{-}O_{(6)}\#2}$	180.0	$\mathrm{Si_{(2)}{-}O_{(3)}{-}Li_{(1)}}$	139.6(3)
$\mathrm{Li_{(2)}\#2{-}Cr_{(2)}{-}Li_{(2)}}$	180.0	$\mathrm{Si_{(2)}{-}O_{(3)}{-}Cr_{(1)}}$	124.0(2)
$\mathrm{O_{(1)}{-}Si_{(1)}{-}O_{(2)}}$	111.3(2)	$\mathrm{Li_{(1)}{-}O_{(3)}{-}Cr_{(1)}}$	90.1(2)
$\mathrm{O_{(3)}{-}Si_{(2)}{-}O_{(2)}}$	110.39(14)	$\mathrm{Si_{(3)}{-}O_{(4)}{-}Li_{(2)}\#2}$	142.4(3)
$\mathrm{O_{(4)}{-}Si_{(3)}{-}O_{(5)}}$	111.5(2)	$\mathrm{Si_{(3)}{-}O_{(4)}{-}Cr_{(2)}}$	126.5(2)
$\mathrm{O_{(6)}{-}Si_{(4)}{-}O_{(5)}}$	110.87(14)	$\mathrm{Li_{(2)}\#2{-}O_{(4)}{-}Cr_{(2)}}$	90.8(2)
$\mathrm{O_{(3)}{-}Li_{(1)}{-}O_{(1)}\#1}$	91.2(3)	$\mathrm{Si_{(4)}{-}O_{(5)}{-}Si_{(3)}}$	126.0(2)
$\mathrm{O_{(3)}{-}Li_{(1)}{-}N_{(2)}}$	121.1(4)	$\mathrm{Si_{(4)}{-}O_{(6)}{-}Li_{(2)}}$	137.7(3)
$\mathrm{O_{(1)}\#1{-}Li_{(1)}{-}N_{(2)}}$	120.1(4)	$\mathrm{Si_{(4)}{-}O_{(6)}{-}Cr_{(2)}}$	126.06(14)
$\mathrm{O_{(3)}{-}Li_{(1)}{-}N_{(1)}}$	112.5(4)	$\mathrm{Li_{(2)}{-}O_{(6)}{-}Cr_{(2)}}$	89.4(2)

Symmetry transformations used to generate equivalent atoms:
#1 $-x+1,-y+1,-z$ #2 $-x+1,-y,-z+1$

in **5**. Also as with **5** the 6- and 8-membered metallasiloxane rings in **2** are relatively planar but the ring twist is 58°. Within the metallasiloxane rings related Si–O bond distances and related angles at silicon and oxygen generally vary in a similar way in both the Co and Mg compounds **2** and **5**. The presence of different metals at spiro sites affects angles within the 8-membered rings to a greater extent. Thus differences between the average Si–O–M angles in the 8-membered rings [134.26(19)° Co, 142.2(2)° Mg] are greater than in the 6-membered rings [120.97(17)° Co, 123.5(2)° Mg]. Likewise for the Si–O–Si angles the differences between the 8-membered rings [150.4(2)°, 156.0(2)° Co and 157.2(2)°, 160.5(2)° Mg] are marked compared to 6-membered rings [131.9(2)° Co and

133.2(2)° Mg]. Bite angles are very similar in both compounds and are wider for the 8-membered ring in both cases as expected. The geometry at lithium atom is very distorted tetrahedral with the (Si)O–Li–O(Si) angles close to 90° compensated by wide O–Li–N(Py) angles (~120°) as in related structures.

Structural Features of $[Cr\{O(Ph_2SiO)_2\}_2\text{-}\mu\text{-}(LiPy_2)_2]$ (3). The molecular structure of **3**, one of two crystallographically distinct but very similar molecules in the unit cell, is shown in Fig. 3. Bond lengths and angles are reported in Table 4. As for the analogous sodium-bridged spirocyclic compound [20] there is square planar geometry at chromium atom in this compound with two coplanar 6-membered chromiasiloxane rings. The bond distances and angles in the central spirocyclic core are apparently unaffected by the change from THF-solvated sodium atom, to pyridine-solvated lithium atom which suggests that the stereochemical requirements of the chromium atom are dominant.

CONCLUSIONS

Our previous work on reactions between metal chlorides and the reagents $[O(Ph_2SiOM)_2]$ (M = Li or Na) suggested that ligand oligomerization or rearrangement was highly dependent on specific target metal centers. The structures we have isolated using $Ph_2Si(OH)_2$/BuLi(1:2) and different metal chlorides show that oligomerization from the silane diolate to disiloxanediolate (trisiloxanediolate in one case) is readily promoted. The ligands $(OSiPh_2OLiOH)^{2-}$, $(OSiPh_2OSiPh_2O)^{2-}$, and $(OSiPh_2OSiPh_2OSiPh_2O)^{2-}$ have been found in metallasiloxane compounds derived from $Ph_2Si(OH)_2$/BuLi (1:2). So far no compound with the simple diolate $Ph_2SiO_2^{2-}$ has been isolated from $Ph_2Si(OH)_2$/BuLi (1:2). In comparison the ligands $(OSiPh_2O)^{2-}$, $(OSiPh_2OSiPh_2O)^{2-}$, and $(OSiPh_2OSiPh_2OSiPh_2OSiPh_2O)^{2-}$ have been found in metallasiloxane compounds derived from the diol $Ph_2Si(OH)_2$. Owing to the ill-defined nature of the reagent $Ph_2Si(OH)_2$/BuLi (1:2) it is not possible to assess whether the target metal center controls the ligand oligomerization or not. However as with metallasiloxanes derived from the well-defined reagent $[O(Ph_2SiOLi)_2]$ there is no evidence for mixtures of metal compounds being formed in reactions between $Ph_2Si(OH)_2$/BuLi (1:2) and metal chlorides and product formation is apparently selective in each case.

EXPERIMENTAL

All manipulations were carried out under dry nitrogen atmosphere using standard Schlenk techniques. The compound $Ph_2Si(OH)_2$ (Aldrich) was heated gently under vacuum for several hours and then stored under nitrogen. IR spectra were recorded using a Perkin-Elmer 1720X spectrometer (either as nujol mulls between CsI plates, or neat with an ATR attachment). The IR spectrum of each of the compounds **1**, **2**, and **3** has a band around 1590 cm^{-1} associated with the phenyl groups present, strong bands in the region of 950 cm^{-1} are attributed unit to stretching and bending in the Si–O–M while overlapping bands in the region 1120-1000 cm^{-1} are due to Si–O–Si stretching and bending. Elemental analyses were obtained from University College London. ^{1}H NMR spectra were recorded on a Bruker WH80 spectrometer with data listed in ppm downfield from $SiMe_4$. ^{29}Si and ^{7}Li NMR spectra were recorded on a Bruker AMX600 spectrometer with data listed in ppm downfield from $SiMe_4$ and LiCl in D_2O, respectively. Compound **5** was prepared as previously described [17].

$[Mg\{O(Ph_2SiO)_2\}_2]\text{-}\mu\text{-}(LiPy)\text{-}\mu\text{-}\{(LiPy)_3(OH)(Cl)\}]$ (1). A solution of $MgCl_2\cdot 2THF$ (0.48 g, 2 mmol) in THF (10 cm^3) was added dropwise to a stirred white suspension from $Ph_2Si(OH)_2$ (2.16 g, 10 mmol) in THF (10 cm^3) and BuLi (12.5 cm^3 of 1.6 mol·dm^{-3} in hexane; 20 mmol) at room temperature. The mixture cleared to pale yellow overnight. The organic solvents were removed and the residual white solid stirred in toluene (30 cm^3). The filtered toluene solution was concentrated to one-third volume and then pyridine added till the solution became turbid (~2 cm^3). Upon heating with an air gun this turbid mixture cleared and on standing at room temperature for 48 h gave colorless crystals (1.87 g, 75% based on magnesium chloride); mp 194-196°C. Found, %: C 64.2; H 5.3, N 3.9. $C_{68}H_{61}N_4O_7Si_4Li_4MgCl$. Calculated, %: C 65.6; H 4.9; N 4.5.

IR spectrum (nujol mull, cm^{-1}): 3400w 1595m, 1581w, 1435s, 1262m, 1118s, 993s, 965s, 801m, 743m, 743s, 625w, 534s.

^{1}H NMR spectrum (C_6D_6, δ): 6.83 (m, 8H, Py); 7.23 (m, 24H, Ph); 7.70 (m, 16H, Ph); 7.85 (m, 4H, Py); 8.00 (m, 8H, Py) (298 K). ^{7}Li NMR spectrum (C_7D_8, δ): 0.36 (s) (297 K). ^{29}Si NMR spectrum (C_7D_8, δ): -41.50 (s) (300K).

To ensure sample homogeneity we took the precaution of measuring unit cells for several crystals from the bulk and in each case these were identical to **1**.

$[\{O(Ph_2SiO)_2\}Co\{O(Ph_2SiO)_3\}\text{-}\mu\text{-}(LiPy_2)_2]$ (2). A stirred suspension from $Ph_2Si(OH)_2$ (2.16 g, 10 mmol) in THF (10 cm^3) and BuLi (12.5 cm^3 of 1.6 mol·dm^{-3} in hexane; 20 mmol) in THF (40 cm^3) was treated at -78°C with solid $CoCl_2$ (0.26 g, 2 mmol), brought gradually to room temperature and stirred for 48 h to give a lilac suspension. The solvent was removed and the residual solid was stirred in hot toluene (50 cm^3) and then filtered. The toluene solution was concentrated and then treated with pyridine as for **1** above. On standing at 5°C for several days dark blue crystals were deposited (1.4 g, 47% based on $CoCl_2$); mp 197°C. Found, %: C 68.1; H 5.1; N 3.5. $C_{87}H_{78}CoLi_2N_4O_7Si_5$. Calculated, %: C 69.4; H 5.2; N 3.7 %.

IR spectrum (cm^{-1}): 2962m, 1592m, 1484w, 1440m, 1426m, 1259s, 1108-976 brs, 870w, 796s, 696s, 529s.

$[Cr\{O(Ph_2SiO)_2\}_2\text{-}\mu\text{-}(LiPy_2)_2]$ (3). The procedure outlined above was carried out with solid $CrCl_2$ (0.25 g, 2 mmol). A purple suspension was obtained when addition of $CrCl_2$ was complete. After further work-up as above dark orange crystals were obtained from green toluene/pyridine solution (1.25g, 52% based on $CrCl_2$); mp 213°C. Found, %: C 65.2; H 5.0; N 3.5. $C_{68}H_{60}CrLi_2N_4O_6Si_4$. Calculated, %. C 67.6; H 5.0; N 4.6.

IR spectrum (cm^{-1}): 3061w, 1593m, 1426m 1110s, 1065w, 1036w, 947s, 740m, 695s, 623w.

$[\{O(Ph_2SiO)_2\}Co\{(OPh_2Si)_3O)_2\}\text{-}\mu\text{-}(CoClPy)_2]\cdot Py$ (4). $CoCl_2$ (1.12 g, 8.68 mmol) in THF (15 cm^3) was added dropwise to a solution of the magnesium compound 5 (4.34 mmol) in THF (40 cm^3). The mixture was stirred for 48 h. Removal of the solvent followed by toluene pyridine work-up as described above gave blue crystals at room temperature (4.2 g, 65%); mp 235-237°C. Lithium flame test negative. Chloride test positive. Found, %: C 60.9; H 4.6; N2.8. $C_{75}H_{65}Co_2Cl_2N_3O_8Si_5Mg$. Calculated, %: C 60.5; H 4.4; N 2.8.

IR spectrum (nujol mull): 1654m, 1607m, 1590w, 1428s, 1304w, 1261m, 1114s, 1069m, 1033s, 1019s, 993s, 929s, 802m, 744s, 717s, 697s, 530s.

X-RAY CRYSTALLOGRAPHY.

Single crystal data. Single crystals were selected from the crops deposited and sealed in glass capillaries under argon without further drying. Cell refinement and data collection were performed on a Enraf-Nonius CAD4 diffractometer operating in the ω/2θ scan mode using CAD-4/PC [22] and data reduction accomplished using XCAD4 [23]. The structures were solved by standard heavy atom techniques (SHELXS-97) and refined by least squares (on F^2) using SHELXL-97 [24]. In the final refinements anisotropic parameters were refined for all non-hydrogen atoms. In each case phenyl groups were treated as rigid hexagons (C–C, 1.395 Å; C–C–C, 120°) and hydrogen atoms were included at fixed positions (C–H, 0.93 Å). Data were corrected for absorption using an empirical method (ψ-scans) [25], with T_{min} = 0.8152, T_{max} = 0.8517 for (1); T_{min} = 0.965, T_{max} = 0.998 for (2) and T_{min} = 0.9543, T_{max} = 1.00 for (3). The molecular plots were produced with ORTEP-3 for windows [26].

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